

The University of Chicago

COLLOIDAL PRIMARY COPPER ORES
AT CORNWALL MINES, SOUTH-
EASTERN MISSOURI

A DISSERTATION SUBMITTED TO THE
FACULTY OF THE DIVISION OF THE
PHYSICAL SCIENCES IN CANDIDACY FOR
THE DEGREE OF DOCTOR OF PHILOSOPHY

DEPARTMENT OF GEOLOGY AND PALEONTOLOGY

1935

By

GEORGE W. RUST

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GEORGE W. RUST
University of Chicago

ABSTRACT

Evidences are cited which indicate a hydrothermal ancestry for the mineralizing solutions. Some of the primary mineral species which suggest such an interpretation are: bornite, enargite, famatinite (?), isometric chalcocite, and primary covellite. Lack of alteration of the wall indicates very moderate temperatures. Several unusual types of structures and textures suggest ore deposition from colloidal solutions. A deep-seated, magmatic source is postulated for these solutions. The proximity of the mines to a major fault belt indicates that these faults may have facilitated the rise of mineralizing solutions from the postulated deep-seated source. The presence, a few miles to the southwest, of igneous intrusives may have significant bearing on the genesis of the ores.

INTRODUCTION

In an extensive literature devoted to the Mississippi Valley ore deposits widely divergent views have been advanced concerning the genesis of the ores. In studying the mineralization at the Cornwall mines the writer hoped to uncover sufficient diagnostic evidence to determine the genesis of the ores at these mines and thus fill a gap in the much larger picture of the Mississippi Valley deposits in general.

The mines are located about 10 miles southwest of the town of Ste Genevieve in southeastern Missouri (Ste Genevieve County) along a small stream tributary to the Rivier aux Vases (Fig. 1). Since 1872, nine years after copper was first discovered, mining has been carried on intermittently. The early history of the mines is given in a brief report by Nicholson.¹ In a more recent description of the workings Weller and St. Clair² reported the property as operating when last visited by them in 1916.

GENERAL GEOLOGY

The mines are situated on the northeast structural slope of the domelike Ozark uplift, the center of which lies about 30 miles to the

¹ Frank Nicholson, "Review of the Ste Genevieve Copper Deposits," *Trans. Amer. Inst. Min. Met. Eng.*, Vol. X (1882), p. 444.

² Stuart Weller and Stuart St. Clair, "Geology of Ste Genevieve County, Missouri," *Mo. Bur. of Geol. and Mines*, Vol. XXII (2d ser., 1928), p. 331.

southwest where pre-Cambrian granite outcrops over large areas. The rock formations involved in the mineralization at the Cornwall mines are the Cotter and Powell dolomites of Lower Ordovician age. For complete detailed description of the stratigraphy the reader is referred to Weller and St. Clair.³ Just south of the mines is a structural belt characterized by a complex mosaic of normal faults which

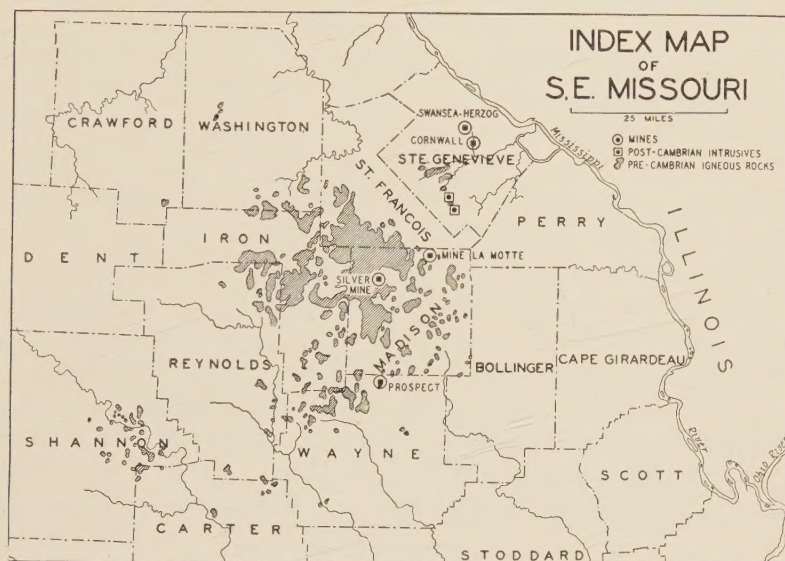


FIG. 1.—Map showing location of Cornwall mines

extends for 50 miles across the central part of Ste Genevieve County from northwest to southeast. Although the mineralization is not within the zone of strong faulting, some minor fractures of small displacement are observed in the mines. The main faulted zone extends southeastward and disappears beneath the flood-plain deposits of the Mississippi River. Its probable continuation may be seen across the river in the southern Illinois fluorspar district where the relations between faulting, igneous activity, and mineralization have been most recently studied by Bastin.⁴

A few miles to the southwest of the Cornwall copper mine, on the

³ *Ibid.*, pp. 81-90.

⁴ Edson S. Bastin, "The Fluorspar Deposits of Hardin and Pope Counties, Illinois," *Ill. Geol. Surv. Bull.* 58 (1931).

opposite side of the fault zone, igneous intrusives cut the sedimentaries. Two of these have been studied in detail by Tarr and Keller,⁵ and by Singewald and Milton.⁶ As yet these have not been conclusively shown to be related to the mineralization of the region. Other intrusives in the locality are being studied.

ENVIRONMENT OF ORE DEPOSITS

GENERAL FEATURES

The ore occurs as irregular, discontinuous, lenticular to pockety blanket deposits, controlled by and developed along essentially horizontal stratigraphic breaks in the massive dolomite beds. The ore seems to be heaviest at the intersection of these horizontal levels, with minor vertical fractures along which some mineralization also has occurred. The vertical offshoots extend as much as 15 feet upward but only a few feet down from the horizontal ore levels.

Workings have been developed along three distinct horizons, and copper sulphides have been reported to occur along four additional levels, one outcropping and the other three revealed by drillings.⁷

While a number of horizons have been mineralized, extensive development has been principally along the stratigraphic break separating the upper and lower Powell members. This level is marked by thin alternating lenses of sandstone, conglomerate, and breccia.

SEQUENCE IN MINERALIZED ZONES

Development of older chert.—The chert of the Powell formation is not confined to the dolomite beds but occurs in considerable amounts as nodules in a sandstone member about 15 feet below the main mineralized level. This variety of chert has heretofore been termed "oolitic" due to the presence of variable amounts of included sand grains. It is being studied in more detail in an effort to confirm the writer's belief that it is syngenetic.

Dolomitization.—There is no apparent genetic relation between dolomitization and mineralization. The magnesium content of the

⁵ W. A. Tarr and W. D. Keller, "A Post-Devonian Igneous Intrusion in Southeastern Missouri," *Jour. Geol.* Vol. XLI (1933), p. 815.

⁶ Joseph T. Singewald, Jr., and Charles Milton, "An Alnoite Pipe, Its Contact Phenomena, and Ore Deposition near Avon, Missouri," *ibid.*, Vol. XXXVIII (1930), p. 54.

⁷ H. Foster Bain and E. O. Ulrich, "The Copper Deposits of Missouri," *U.S. Geol. Surv. Bull.* 267 (1905), p. 39.

Powell dolomite seems to be very uniform. Variation in crystallinity of the dolomite is not related to amount or locus of mineralization. Included fragments of dolomite in the heavily mineralized breccia are no more coarsely crystalline than elsewhere, as they should be if dolomitization were due to the mineralizing solutions.

Period of solution.—The breccia portions of the principal ore level have been interpreted by Weller and St. Clair⁸ as being in part sedimentary in origin. The writer would recognize three breccia types, gradational with one another and all traceable in origin to extensive solution of the dolomite at the ore level. This solution, guided by, and advancing upward from, the original stratigraphic break, progressed unequally, resulting in large semicircular pockets up to 20 feet in diameter above the mineralized level. Subsequent collapse of a supporting column between adjacent solution pockets here and there has developed considerable crush breccia, some of which was modified by continued solution with the complete elimination of the dolomite and the further incorporation of the broken chert fragments in a fine, siliceous, insoluble residue. Silicification (chertification) of this matrix residue has resulted in a hard breccia composed entirely of chert (Fig. 2, 4). This second-generation chert is apparently related to the mineralization. Nicholson⁹ has illustrated and described the results of this solution in some detail.

PRIMARY MINERALIZATION

REPLACEMENT VERSUS FILLING OF OPENINGS

Compared to the total ore, the amount of sulphide ore directly and completely replacing dolomite is small. A large amount of dolomite has been removed and a smaller amount of sulphide deposited, but most of the sulphide does not show distinctive evidence of having been formed by replacement; instead, it seems to have filled open spaces already existent, such as spaces between sand grains and breccia fragments and vugs of highly porous dolomite. In those specimens which seem to show evidence of direct dolomite replacement by sulphides (Fig. 8, 5), the percentage of dolomite within the sulphide area is nearly equal in many cases to the percentage be-

⁸ *Op. cit.*, p. 333.

⁹ *Op. cit.*, pp. 450-53.

yond the sulphide frontier (Fig. 8, 4). Porosity in the dolomite is greatest near the sulphide area and decreases away from it. It is believed that this condition was caused by the incomplete solvent action of the mineralizing solutions advancing along grain boundaries. The sulphides, after coagulation and under the influence of surface

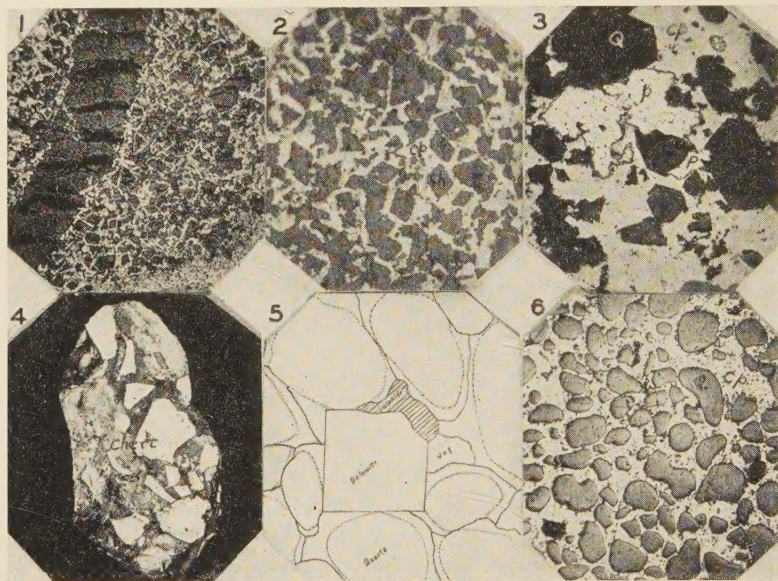


FIG. 2, ILLUSTRATIONS 1-6.—*Cp*, chalcopyrite; *Ch*, chert; *P*, pyrite; *Q*, quartz. 1. $\times 15$. Chert pseudomorphic after dolomite. Note open shrinkage cracks developed in chert areas after the introduction of the chalcopyrite. 2. $\times 56$. Same as 1. 3. $\times 40$. Quartz crystals developed by secondary addition rims on rounded sand grains. Note that quartz conforms to pyrite, which in turn conforms to original outline of rounded sand grain. 4. $\times \frac{2}{5}$. Two generations of chert with breccia structure. The second generation (matrix) chert has developed by silicification of a very fine insoluble silica residue resulting from solution of the Powell dolomite. 5. $\times 64$. Dolomite crystals embedded in sandstone and automorphic toward secondary silica addition rims. 6. $\times 15$. Mineralized sandstone. Note separation of sand grains without replacement. In other less conservative fields the space between sand grains is as much as ten times the diameter of the largest sand grain. These mineralized areas are completely surrounded by unmineralized but silicified sandstone.

tension of the resulting gelatinous mass, were concentrated into a central zone in the total area affected by the solvent action of the disperse colloidal solutions.

COLLOIDAL VERSUS ELECTROLYTIC DEPOSITION

A wide variety of characteristic textures indicates clearly the colloidal condition of the ore material at the time of deposition. These textures are not limited to one or two species, but involve most of the primary minerals. Some of the textures and structures are widely

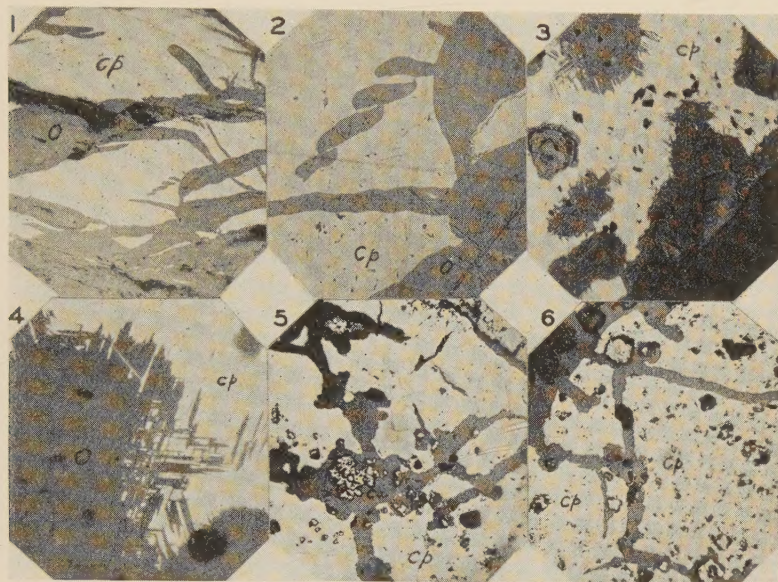


FIG. 3, ILLUSTRATIONS 1-6.—*Cp*, chalcopyrite; *O*, intimate mixture of oxides of iron and copper; *Ma*, malachite; *Ca*, calcite; *P*, pyrite. 1. $\times 20$. Intimate mixture of copper and iron oxides replacing primary chalcopyrite. Note gross, clublike forms with smooth contacts as contrasted with characteristic ragged electrolytic replacement frontiers. These secondary oxides are believed to be colloidal in origin but not necessarily related to the primary colloidal sulphide deposition. 2. $\times 100$. Same as 1. 3. $\times 75$. Replacement frontiers of secondary oxides controlled by crystallographic directions of host mineral—chalcopyrite. Malachite replaces the oxides. 4. $\times 208$. Same as 3. 5. and 6. $\times 31$. Calcite selectively replacing chalcopyrite and leaving pyrite. This replacement preceded enrichment.

accepted as characteristic of colloiddally deposited material. Other no less well-defined textures, heretofore not recognized as colloidal in origin, have been so interpreted by the writer and are submitted for consideration as valuable additional criteria to be added to the scanty list of recognized colloidal textures now available. Some of

the most distinctive and most frequently occurring colloiddally interpreted textures are described below.

1. Concentric, colloform structures. These are marked by (1) concentric shrinkage cracks in a single mineral (Fig. 4, 1); (2) alternating bands of two different minerals as in Figure 4, 3; (3) the

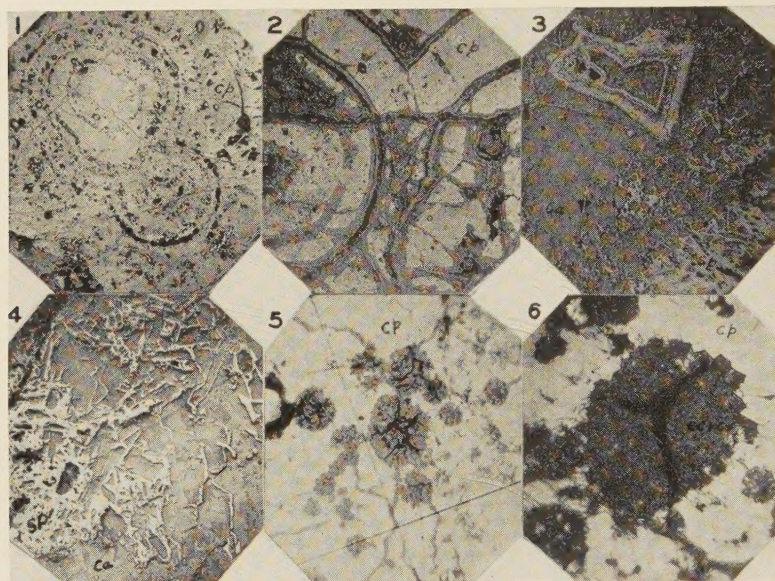


FIG. 4, ILLUSTRATIONS 1-6.—*Cp*, chalcopyrite; *O*, intimate mixture of copper and iron oxides; *Ca*, calcite; *Sp*, sphalerite; *Cc*, chalcocite; *Co*, covellite. 1. $\times 25$. Colloform banding in primary chalcopyrite. Small white grains with high relief are pyrite; black areas are vugs. 2. $\times 15$. Colloform structures in primary ore controlling the development of secondary oxides. 3. $\times 40$. Alternating bands of calcite and sphalerite. These are believed to be essentially contemporaneous in age. 4. $\times 32$. Different field of same specimen as 3. Under higher magnification many perfect crystals of calcite are seen to be entirely enclosed in sphalerite. 5. $\times 200$. Globules of an intimate mixture of primary isometric chalcocite and covellite showing cracked porcelain texture. 6. $\times 400$. Septaria shrinkage cracks developed in ex-solution(?) mixture of isometric chalcocite, and covellite. Same specimen as 5. Note crystal faces of chalcopyrite against the globule.

controlling influence of inconspicuous primary structures on the development of secondary sulphides (Fig. 4, 2); and (4) structures which, if not already visible, may be discovered by etching with acid fumes.

2. Syneresis shrinkage cracks. These may be classified into (1) "septaria" type of shrinkage expression involving small globular areas of one or two minerals (Fig. 4, 6), or larger circular areas containing several minerals (Fig. 5, 3, 4, 5, and 6), (2) cracked porcelain textures mentioned by Lindgren¹⁰ as being colloidal in origin (shown

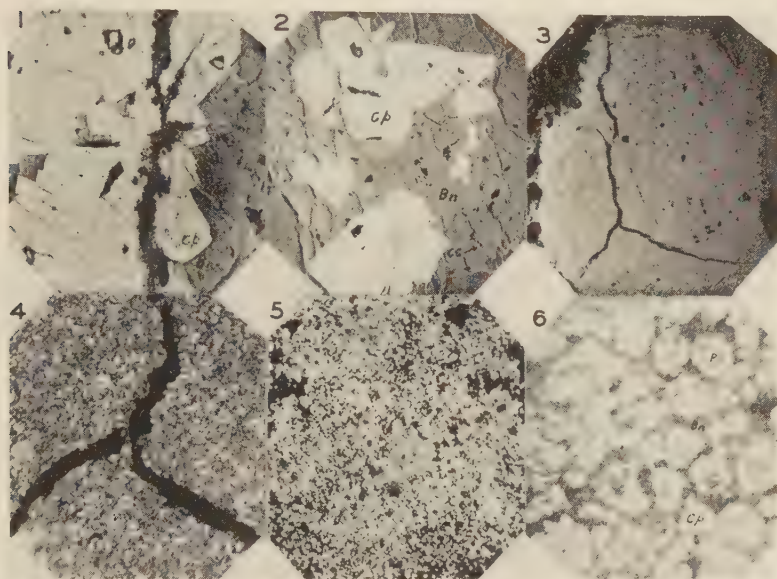


FIG. 5, ILLUSTRATIONS 1-6.—*Cp*, chalcopyrite; *Bn*, bornite; *Cc*, chalcocite; *P*, pyrite. 1. $\times 32$. Primary bornite, interstitial toward automorphic chalcopyrite. 2. $\times 30$. Chalcopyrite crystals in primary bornite. Secondary chalcocite veinlets selectively replacing bornite. 3. $\times 10$. Septaria shrinkage cracks developed in a circular sulphide area (replacing dolomite pebble in sandstone). The cracks cut an intimate mixture of three primary minerals (see 4, 5, and 6). 4. $\times 40$. Same as 3, higher magnification. 5. $\times 60$. Less altered field of same specimen as seen in 3 and 4. 6. $\times 550$. Same as 5, high magnification. Note pyrite cores and bornite matrix to chalcopyrite spherules. Bornite partially replaced by secondary chalcocite (dark gray to black).

in small scale in Fig. 4, 5); (3) lenticular syneresis cracks in definite angle "grid" pattern (Fig. 6, 5). The cause of this pattern is not known, but it seems possible to the writer that it may be in part external and due to rotational stress applied to a semi-rigid con-

¹⁰ Waldemar Lindgren, *Mineral Deposits* (4th ed.), p. 842.

tracting gel mass.¹¹ If the extensive solution at the mineralized horizon was accomplished by the mineralizing solutions, we can easily imagine unequal stress resulting from collapse. The lenticular character of the cracks is to be emphasized. (4) Lenticular cracks which

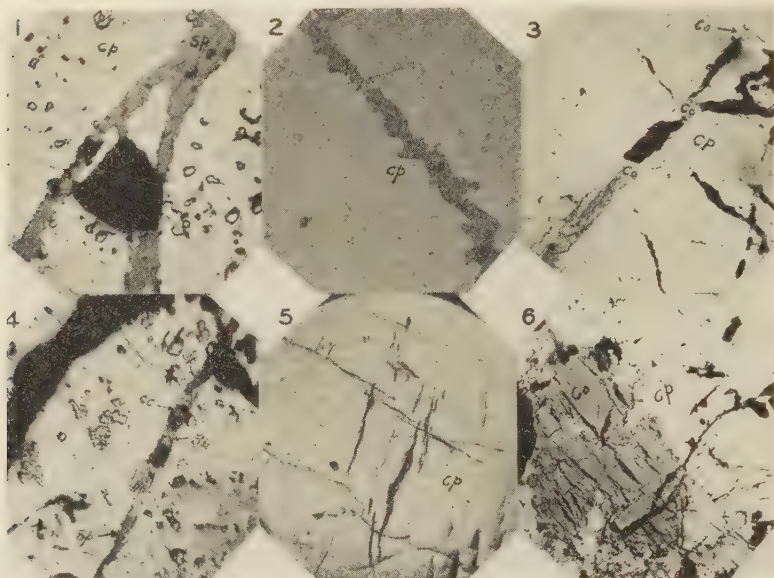


FIG. 6, ILLUSTRATIONS 1-6.—*Cp*, chalcopyrite; *Sp*, sphalerite; *Co*, covellite; *Cc*, chalcocite; *Bn*, bornite. 1. $\times 52$. Sphalerite veinlets cutting chalcopyrite and showing crystal faces of host against guest. 2. $\times 240$. Same as 1. This type of veinlet is believed to have been formed by injection of sphalerite along shrinkage or rupture fractures in semi-rigid chalcopyrite gel, with subsequent crystallization and development of crystal faces of chalcopyrite against the later sphalerite. 3. $\times 40$. Segmented veinlets of primary covellite alternating with open cracks (see 4). 4. $\times 40$. Segmented veinlets. Alternating segments of sphalerite, bornite, chalcocite, and open vugs. This type of veinlet is believed to have been formed by expulsion of the disperse phase as chalcopyrite gel shrunk and formed cracks. Coagulation and contraction of the disperse material in the cracks caused segments of different minerals to alternate with each other and with vugs. This segmentation is an expression of selective coagulation of different disperse materials. 5. $\times 10$. Lenticular syneresis cracks with a definite angular orientation. 6. $\times 50$. Syneresis cracks controlled by the crystallographic directions in primary covellite.

have no definite orientation; and (5) lenticular cracks which may have a crystallographic control (Fig. 6, 6).

¹¹ The writer is aware that sulphide coagulums are not true gels but better termed "gelatinous precipitates." Behavior of these precipitates after flocculation, however, follows closely the habits of gels. For simplicity, then, they will be spoken of as "gels."

3. "Framboidal"¹² clusters of tiny pyrite cubes and grains, the whole with a spheroidal outline. In some cases the grains have a matrix of primary chalcopyrite (Fig. 7, 4), and in other cases the matrix is secondary (Fig. 7, 2 and 3). In Figure 7, 1, the spheroids

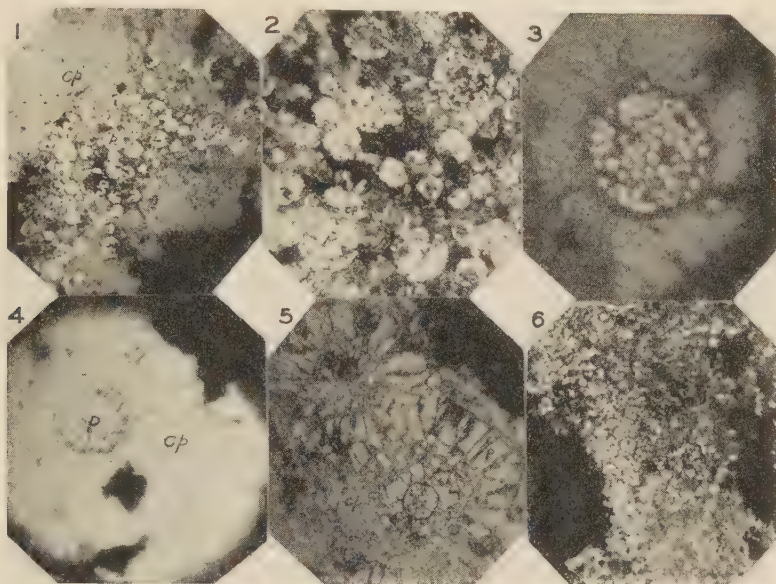


FIG. 7, ILLUSTRATIONS 1-6.—*Cp*, chalcopyrite; *P*, pyrite. 1. $\times 108$. Solid spheroidal masses of pyrite in chalcopyrite. 2. $\times 166$. "Framboidal" spheroidal masses of pyrite in chalcopyrite due to metacolloidal crystallization. 3. $\times 580$. "Framboidal" clusters of pyrite grains due to crystallization of a gel globule. Secondary minerals separate the discrete crystals of pyrite. 4. $\times 450$. Same as 3 except that there has been no enrichment of the ore and hence chalcopyrite still forms the matrix of the pyrite cubes and grains. 5. $\times 400$. Radial "bomb" type of texture developed in pyrite with a small "framboidal" nest of pyrite grains in the center of one pyrite area. Chalcopyrite matrix of "bomb" fragments. 6. $\times 64$. Spheroidal globules of chalcopyrite, with pyrite core, and chalcocite (after bornite) matrix.

are composed of solid pyrite. There are present complete gradations between the solid spheroids and globules composed entirely of tiny uniform-sized pyrite cubes. These are probably metacolloidal in origin, having been formed by the crystallization of a globule of pyrite gel, crystallization starting at many points at the same time. In an alternative hypothesis, the texture might be considered to have

¹² After *framboise* (Fr.) for "raspberry."

been formed by the bunching of tiny pyrite grains as they floated in a chalcopyrite gel. On the basis of uniformity of grain size, gradational types between the grain clusters and solid spheroids, and the fact that in non-circular, irregular pyrite masses, the "framboidal" texture may be produced artificially by etching with nitric acid, the writer prefers the former interpretation.

4. "Frog-egg"¹³ masses of chalcopyrite with pyrite cores, the whole implanted in a matrix of primary bornite and its alteration product chalcocite (Fig. 5, 5 and 6, and Fig. 7, 6).

5. Pyrite occasionally shows a radial habit with a nest of "framboidal" granules as a core (Fig. 7, 5).

6. Veinlets of a late primary mineral cutting an earlier primary mineral with the walls of the veinlet composed of automorphic crystal faces of the host projecting into the guest (Fig. 6, 1 and 2). These veinlets are believed to have formed by fracturing of a semi-rigid gel, either by shrinkage or by distortion, followed by injection of later colloidal material and subsequent crystallization of both with the host mineral assuming euhedral relations against the vein material.¹⁴

7. Segmented veinlets. The above-described veinlets, consisting dominantly of sphalerite, are interrupted in places by segments of bornite, chalcocite, and by open gaps, alternating along the course of the veinlets (Fig. 6, 4). In another specimen lenticular shrinkage cracks are partially filled with covellite, constituting abrupt covellite segments alternating with gaps (Fig. 6, 3). The coagulation of a disperse colloid to form a gel is followed by contraction (syneresis) with the expulsion of the disperse medium.¹⁵ In the case of selective coagulation, the expelled disperse phase might be expected to carry

¹³ Term suggested as descriptive of this peculiar texture as shown in Fig. 5, 5 and 6. Note chalcopyrite spheroids carry a pyrite kernel and are enveloped in a bornite medium, an arrangement not unlike clusters of frog eggs.

¹⁴ In a conversation between the writer and Dr. E. S. Bastin the latter agreed with the writer's interpretation and pointed out the similarity between these veinlets and some noted by him in ores from Cobalt, Ontario, and expressed the belief that the Cobalt occurrence should be explained in the same way. This agrees with the opinion of Lindgren in his paper on "Metasomatism," *Geol. Soc. Amer. Bull.* 36 (1925), pp. 247-62, in which he expressed the belief that the Cobalt ores were colloiddally deposited.

¹⁵ H. R. Kruyt and H. S. van Klooster, *Colloids* (1930), p. 250.

considerable disperse colloidal matter which would be confined to the shrinkage crack. When this vein material coagulated, it would likewise contract and only locally fill the original shrinkage crack. If more than one mineral had been left in the original expelled disperse medium, the minerals would alternate with each other and with gaps formed by shrinkage of the vein material. If we could see these segmented veinlets sectioned in the plane of the original shrinkage crack, we would doubtless note circular globules of the different minerals separated by considerable vug space. This arrangement tells us nothing of the relative ages (order of coagulation) of the different minerals in the cracks.

8. In the case of the mineralized sandstones and also the chert nodules formed in sandstone, the sand grains are notably separated (Fig. 2, *δ*). There has been no replacement of the sand grains, and yet in extreme cases the grains are separated by an amount equal to several times their diameter. The cause of this separation is not entirely clear. It seems probable that the explanation is to be sought in the gel nature of the matrix material. Whether it be expansion due to crystallization, expulsion of sand grains during contraction of the gel, or selective replacement of an earlier matrix of the sand, is not clear. Beyond the sulphide frontier, the sand grains are in close contact. The writer is inclined to think it is a colloidal phenomenon but would hesitate at the present time to offer it as a criterion for such origin.

9. Under descriptions of individual mineral species, evidence will be presented bearing on the relative order of coagulation of those species. This order is believed to be an expression of the disperse colloidal condition at the time of introduction (see general conclusions).

10. Replacement frontiers of sulphides invading dolomites are characteristically bulbous, mamillary, or nodular in appearance (Fig. 8, *5*). This feature is to be contrasted with typical ragged, feathery replacement frontiers developed by electrolytic replacement. The explanation probably lies in the effect of the high surface tension of gels causing rounded smooth contacts with the invaded rock.

THE PRIMARY ORE MINERALS

The primary ore of the Cornwall mines and vicinity consists dominantly of the sulphides of copper, iron, and zinc, named in order of relative abundance. Of the primary mineral species identified, chalcopyrite is by far the most abundant. Primary minerals occurring

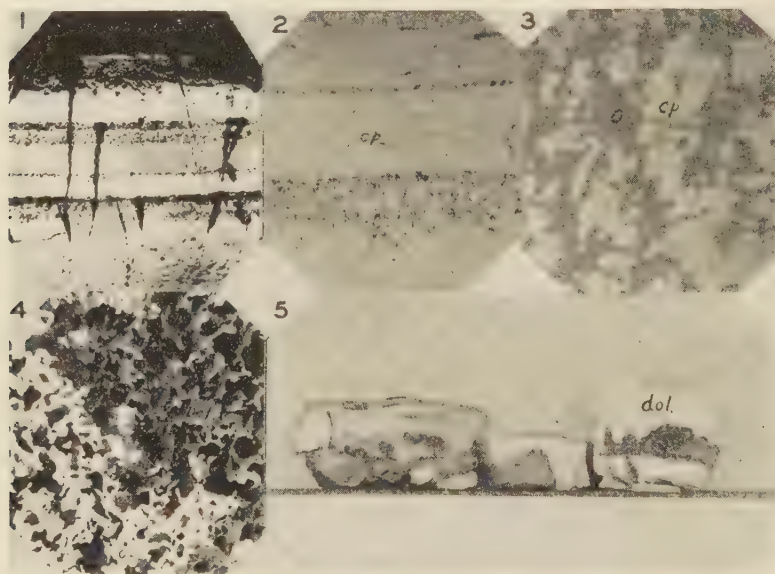


FIG. 8, ILLUSTRATIONS 1-5.—*Cp*, chalcopyrite; *O*, oxides of copper and iron; *Dol*, dolomite; *S*, primary sulphides. 1. $\times 12$. "Mud-crack" type of shrinkage fractures developed in successive bands of chalcopyrite which was deposited on the wall of a fracture in dolomite rock (see 2 and 3). 2. $\times 40$. Higher magnification of bands seen in 1. See 3 and section in text on covellite for detailed explanation. 3. $\times 292$. High magnification of mottled bands seen in 1 and 2. These darker oxide areas are dotted with replacement remnants of covellite and famatinite. This is believed to be essentially a primary texture. 4. $\times 12$. Characteristic porous dolomite beyond sulphide frontiers. Porosity developed by the action of the disperse solutions, but vacated by the contraction of the coagulated gel equivalent. 5. $\times \frac{1}{2}$. Bulbous, gel type of replacement frontier of primary chalcopyrite invading dolomite. Note gray tinge to the sulphide areas due to high dolomite content as seen in 4.

in lesser but important amounts, named in order of relative abundance, are: quartz, pyrite, sphalerite, marcasite, bornite, calcite, and dolomite. Rare occurrences of primary enargite, famatinite (?), chalcocite, covellite, galena, and fluorite were also noted.

Pyrite.—This mineral is rather uniformly scattered throughout the heavier ore as well as the slightly mineralized wall rock. Various types of occurrence include mosaic, coarsely crystalline intergrowth with marcasite, individual isolated euhedral cubes of variable size, individual grains with irregular outlines, solid masses with spheroidal

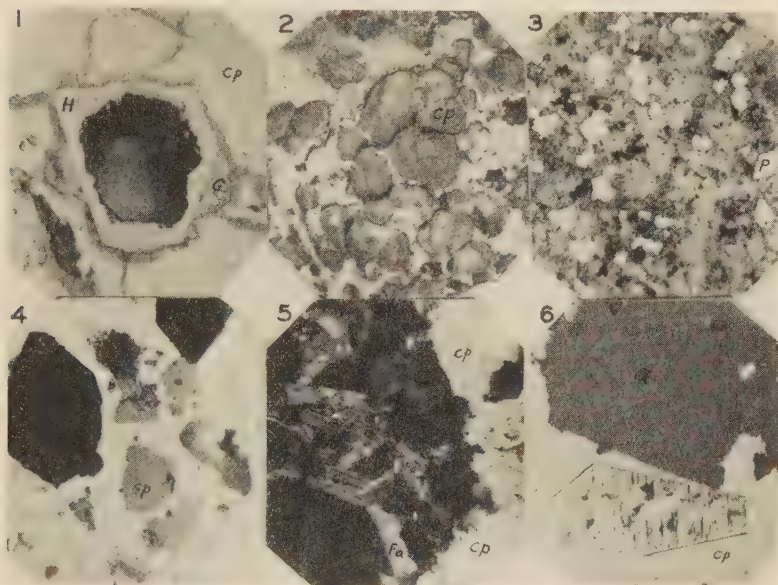


FIG. 9, ILLUSTRATIONS 1-6.—*Cp*, chalcopyrite; *H*, hematite; *G*, goethite; *P*, pyrite; *Sp*, sphalerite; *Q*, quartz; *Co*, covellite; *Fa*, famatinite. 1. $\times 125$. Secondary hematite, pseudomorph after pyrite and coated with drusy crystals of goethite. 2. $\times 2\frac{1}{2}$. Botryoidal chalcopyrite surfaces. 3. $\times 160$. Irregular pyrite grains scattered through chalcopyrite. 4. $\times 150$. Automorphic sphalerite crystals in chalcopyrite. This is in contrast to most sphalerite, which is later and conforms to chalcopyrite. 5. $\times 140$. Intergrowth of crystals of covellite and famatinite (?). 6. $\times 100$. Skeleton crystals of famatinite (?) in chalcopyrite.

outlines, “framboidal” clusters with spheroidal outlines, and radial spheroidal masses with or without “framboidal” cores. Perfect examples of the “framboidal” clusters may be developed by etching with nitric acid an irregular, apparently solid pyrite area, such as shown in Figure 9, 3. Etching of the automorphic pyrite does not produce the granular texture. Gradational types between the solid spheroidal masses, the radial spheroidal masses, and typical “fram-

boidal" masses are quite common, and all these types are thought to represent ore which has crystallized from a gel condition. The automorphic pyrite is probably earlier than the chalcopyrite in which it occurs and probably represents preliminary sulphide deposition directly from the disperse phase before the proper electrolytic concentration had become sufficiently high to cause rapid flocculation and resulting gel textures. Pyrite is notably lacking in all sphalerite and calcite areas. See the section on colloidal textures and the illustrations for further information on pyrite occurrences.

Marcasite.—Types of marcasite occurrence include mosaic; crystalline; pre-gel intergrowth with pyrite and automorphic toward chalcopyrite; radial spheroidal masses implanted in chalcopyrite; and large radial, reniform masses in soft cherts and breccias and not closely associated with other sulphides.

Chalcopyrite.—This is by far the most abundant primary mineral. In the more massive type of occurrence it is dotted with pyrite and quartz grains. Where closely associated with other sulphides the textural relationships may be extremely intimate and characterized by spheroidal globules of chalcopyrite, many of which have "fram-boidal" clusters or irregular pyrite grains as a kernel. The circular globules of chalcopyrite are implanted in a groundmass of primary bornite. This arrangement would seem to suggest the order of coagulation or at least of crystallization as being pyrite, chalcopyrite, and bornite. A much coarser texture involving these three minerals in the same age relationship is seen in Figure 5, 1 and 2. Here again pyrite is automorphic (not well shown in the pictures) and bornite is quasi-interstitial toward chalcopyrite.

Quartz.—Quartz is seen abundantly scattered through the ore as large hexagonal crystals with rounded sand-grain centers, as cryptocrystalline quartz rhombs, pseudomorphic after dolomite, and as finely crystalline quartz matrix (second generation chert) of an older chert breccia (Fig. 2, 1, 2, 3, and 4).

Sphalerite.—Very small amounts of sphalerite were noted as automorphic crystals implanted in massive chalcopyrite and as tiny drusy crystals lining vugs and cracks in the breccia (Fig. 9, 4). Elsewhere massive sphalerite is seen as impregnation of porous dolomite and breccia and as veinlets cutting chalcopyrite as shown in Figure 6, 1 and 2, and discussed under the section on colloidal textures.

Bornite.—This mineral occurs in small amounts but its presence is significant. It shows definite primary relationships with chalcopyrite (Fig. 5, 1, 2, 5, and 6). For further descriptions of its occurrence see the section on colloidal textures and the paragraph on chalcopyrite.

Calcite.—Normally calcite is seen replacing dolomite rock and lining cavities as drusy crystals. In an abnormal occurrence it has formed replacement veinlets in chalcopyrite. (Fig. 3, 5 and 6). There is present a progressive sequence of crystal forms in the drusy calcite. At one end of the series, acute scalenohedrons are dominant. Later this type gradually gives way to rhombohedral forms with an acute rhombohedron as the final end member. Since this last acute rhombohedron was preceded by oxidation, it was probably deposited from descending solutions. According to Kalk,¹⁶ this gradual change in crystal forms is to be expected as an accompaniment of temperature drop, the acute scalenohedral form representing low hydrothermal conditions.

Enargite.—This mineral is found only in very minor amounts, but has been identified in two closely related types of occurrence—as crystals lining vugs and as small isolated crystals enclosed in calcite areas. Identification by microchemical tests was checked by an X-ray spectroscopic analysis.¹⁷

Chalcocite.—In addition to the usual secondary orthorhombic chalcocite, there occur small amounts of primary isometric chalcocite in association with covellite, bornite, and sphalerite along segmented veinlets described under colloidal textures. In an equally characteristic occurrence it is noted as small spheroidal masses dotted with covellite blades and cut by septaria and cracked porcelain textures. Contacts between chalcocite and chalcopyrite are composed in large part of crystal faces of chalcopyrite (Fig. 4, 6). Textural relationships between isometric chalcocite and covellite suggest ex-solution.¹⁸ Experimental work by Pöšnjak, Allen, and

¹⁶ Georg Von Kalk, "Die Kristalltracht des Kalkspates in Minerogenetischer Betrachtung," *Centralblatt f. Min. Geol. u. Pal.*, Part A (1928), pp. 337-39.

¹⁷ See acknowledgments.

¹⁸ Alan Bateman and Samuel G. Lasky, "Covellite-Chalcocite Solid Solution and Ex-solution," *Econ. Geol.*, Vol. XXVII, pp. 52-86.

Merwin¹⁹ seems to have established the fact that chalcocite forming above 91° C. assumes the isometric form and that the presence of 8 per cent or more of dissolved covellite will prevent inversion to the orthorhombic form. This low temperature agrees with the evidence for hydrothermal origin of the solutions as well as the lack of alteration of the wall rock.

Covellite.—Primary covellite is minor in amount, but does occur in the ex-solution type of texture mentioned above as isolated grains in sharp contact with chalcopyrite, in segmented veinlets in chalcopyrite (not replacement veinlets), and as small automorphic grains intergrown with famatinite (?) (see illustrations).

Perhaps the most unusual occurrence of covellite, and the most unusual textural relationship in a deposit replete with extraordinary textures, is what may be termed a colloidal “graphic-like” intergrowth of covellite (now largely replaced by oxides) and chalcopyrite. The intimate intergrowth areas occur as bands which transect the specimen parallel to the surface of the chalcopyrite, which itself is cut by a “mud-crack” type of shrinkage expression (Fig. 8, 1, 2, and 3). These mottled intergrowth bands are believed to represent periods during ore deposition when the carbonate content of the solutions became high enough to cause flocculation of the less easily coagulated covellite²⁰ along with chalcopyrite. Owing to fluctuation of introduction of mineralizing solutions, pure chalcopyrite was flocculated at certain times, and covellite and chalcopyrite were flocculated simultaneously at other intervening times. This explains why the mottled bands come on gradually and end abruptly when the delicate electrolytic balance was upset by a fresh surge of mineralizing solutions. At such a time chalcopyrite deposition continued or was soon resumed.

Famatinite.—This mineral, occurring in small amounts, has not been conclusively identified. It may be the pink variety of enargite known as luzonite. In view of its age difference and mode of occur-

¹⁹ E. Pösnjak, E. T. Allen, and H. E. Merwin, “The Sulphides of Copper,” *ibid.*, Vol. X (1915), pp. 491–535.

²⁰ C. F. Tolman and J. D. Clark, “Copper Sulphides from Colloidal Suspensions,” *ibid.*, Vol. IX (1914), p. 576; J. D. Clark and P. H. Menaul, “Rôle of Colloidal Migration in Ore Deposits,” *ibid.*, Vol. XI (1916), pp. 37–41.

rence, however, it is believed to be famatinite. While it may be seen in almost any specimen, it could not be isolated in sufficient quantities to make a positive identification. In its most characteristic occurrence it is observed as skeleton crystals in chalcopyrite (Fig. 9, 6). It also occurs intimately intergrown with crystals of what is believed to be primary covellite (Fig. 9, 5).

MODIFICATIONS BY SECONDARY ENRICHMENT

While secondary minerals occur in considerable amounts, little or no enrichment has occurred. This fact is probably largely due to the attitude of the ore bodies—dominantly horizontal with minor vertical offshoots of small dimensions.

Secondary minerals that have been identified include chalcocite, covellite, hematite, goethite, cuprite, malachite, smithsonite, cerussite and gypsum. At the upper mineralized level secondary alteration has followed the more usual habits of electrolytic solutions affecting copper-iron sulphides. At the lower horizon, however, the replacement frontiers are sharply contrasted with normal electrolytic replacement contacts (Fig. 3, 1 and 2). These gross, clublike forms with rounded, smooth contacts are believed to be deposited from colloidal solutions. This is borne out by microchemical and microscopic studies, which seem to indicate intimate mixtures of copper and iron oxides for these secondary minerals replacing chalcopyrite directly.

CONCLUSIONS

ORIGIN OF SOLUTIONS

The deposit is interpreted as one of hydrothermal origin, so far removed from the parent igneous source that the temperature at the time and place of deposition had dropped nearly to that of ground waters. Mineral species, however, prove thermal ancestry. The unusually low temperatures account for the scarcity of high-temperature mineral species in the ore as well as the lack of influence of the solutions on the wall rock.

Positive evidence for the hydrothermal origin of the solutions is not overwhelming. A number of converging, though singly not conclusive, lines of evidence, however, seem to support this interpretation. Some of the facts which have been mentioned, and which sug-

gest an igneous ancestry, are: (1) primary bornite; (2) occurrences of enargite; (3) occurrences of probable famatinite; (4) good evidence of primary isometric chalcocite; (5) chalcocite-covellite solid solution and ex-solution textures; (6) primary covellite; and (7) sequence of calcite crystal forms.

ORE DEPOSITION

The mineral succession tables listed below are based on the more usual criteria for the determination of age relations. The writer wishes to point out, however, that this is not a usual type of mineral introduction, and age relations and criteria for the determination of age relations may not hold. In the opinion of the writer, the ores were introduced as dispersed and intimately diffused colloids of different mineral species and flocculation and a gel condition resulted. Order of flocculation of mineral species from such an intimate colloidal mixture would be a specific property of the mineral in question rather than an indication of the order of introduction.

In the case of the injection veinlets of sphalerite cutting chalcopyrite (Fig. 6, 1 and 2), there can be no doubt that the vein material was formed late, though it is not entirely clear whether this age difference is an expression of the late flocculation or late introduction. Crystallization of the host from a gel condition undoubtedly occurred after the injection of the guest. With the possible exception of calcite, sphalerite, and enargite, the writer believes that all of the materials now associated were introduced as a colloidal mixture at the same time, and that their present apparent age relationships are an expression of the order of ease of coagulation of species from that common mixture rather than an indication of the relative period of introduction. Experimental work by Tolman and Clark²¹ and Clark and Menaul²² suggested that certain sulphides coagulate from a dispersed colloidal condition in a definite order, that order being the reverse of ease of dispersion. Several of the copper sulphides studied by them occur in the Cornwall ores and in definite age relations. The order of age of these is pyrite, chalcopyrite, bornite, supposed famatinite, covellite, chalcocite. It is significant that this is the order of coagulation of these minerals as determined by the above-mentioned

²¹ *Op. cit.*

²² *Op. cit.*

experimental workers, with the exception of famatinite, which takes the position of enargite. At the Cornwall mines enargite is intergrown with calcite and is quite late in development. It does not, however, show any evidence of having been deposited from colloidal condition. Its late age may be due to the fact that it was deposited from a true solution along with calcite. Primary galena occurs but in such small amounts that its age relations with respect to the dominant sulphides could not be determined.

In interpreting the age relations of the primary mineral species, two mineral succession tables were used. This seemed necessary in view of the colloidal origin and the resulting gel condition which obtained. The first table gives the ages with respect to the time of introduction; the second is in terms of period of flocculation from colloidal condition.

ORDER OF INTRODUCTION

Pyrite	_____
Marcasite	_____
Chalcopyrite	_____
Bornite	_____
Quartz	_____
Covellite	_____
Chalcocite	_____
Famatinite	_____
Sphalerite	
Enargite	
Calcite	

ORDER OF FLOCCULATION

Pyrite	_____
Marcasite	_____
Chalcopyrite	_____
Bornite	_____
Covellite	_____
Chalcocite	_____
Famatinite	_____
Quartz	_____
Sphalerite	_____
*Enargite	
*Calcite	_____

* May have been deposited from true solutions.

These succession tables were prepared with very great care after many specimens had been studied. While the tables are significant and tend to throw light on the general problem, the conclusions drawn therefrom must be made, as stated above, with recognition of the colloidal condition at the time of introduction. An interesting speculation arises when an attempt is made to offer an explanation of the observed order of flocculation of different mineral species from the disperse condition. Cox, Dean, and Gottschalk²³ believe the order is in the main due to degree of dispersion, but is influenced by many other factors. The order of flocculation determined experimentally by Tolman and Clark and Clark and Menaul was verified by Lasky²⁴ at Kennecott in the Copper River district of Alaska, and by the writer at the Cornwall mines. If degree of dispersion determines the order of flocculation, it is difficult to understand the coincidence of age relations between two naturally occurring, unrelated mineral suites, and between those and laboratory determinations on the same suite of minerals. It also seems more than mere coincidence that the order should be that of decreasing iron and increasing copper content in the mineral compositions. It seems probable that the order of flocculation is closely tied up with the charge on the disperse particles and the relation between that charge and the copper-to-iron ratio in those particles.

Summary of evidence for colloidal deposition.—1. Concentric, colloform structures.

2. "Syneresis" shrinkage cracks, septaria structures, cracked porcelain textures, etc.

3. "Framboidal" clusters and similar related pyrite habits and textures, such as radial pyrite.

4. Globular areas of chalcopyrite with pyrite cores, the whole occurring in a groundmass of bornite ("frog-egg" texture).

5. Veinlets with crystalline borders.

6. Segmented veinlets.

²³ Cox, Dean, and Gottschalk, "Studies on the Origin of the Missouri Cherts and Zinc Ores," *Univ. of Mo. School of Mines and Met., Tech. Series*, Vol. III, No. 2 (1916), p. 25.

²⁴ S. G. Lasky, "A Colloidal Origin of Some of the Kennecott Ore Minerals," *Econ. Geol.*, Vol. XXV (1930), p. 737.

7. Separation and pushing apart of sand grains.
8. Coincidence of order of coagulation and order determined experimentally.
9. Nodular, bulbous, or mamillary replacement frontiers.
10. Banded, colloidal "graphic-like textures."

CHARACTER OF SOLUTIONS

Some suggestion as to the probable nature of the mineralizing solutions is afforded by the consideration of certain facts. The amount of solution of the wall rock (dolomite) connected with the mineralization suggests the possibility that the solutions may have been slightly acidic. The original dispersed condition of the sulphides was probably due to and maintained by the presence of an excess of hydrogen sulphide.²⁵ In certain cases owing to hydrolysis, hydrogen sulphide solutions are alkaline in reaction. In regard to carbonate, however, hydrogen sulphide in solution acts like an acid. The acid condition of the solutions due to an excess of hydrogen sulphide may reasonably have been a retention of conditions existing when the solutions left the magmatic source. Ore-bearing, hydrogen-sulphide-charged emanations from magmatic sources are not uncommon. Clark and Menaul also showed that mineral colloids dispersed by H_2S were precipitated by a piece of calcite when that mineral was suspended in the solutions. The writer noted at the Cornwall mines, in a few specimens of chert breccia carrying an occasional fragment of dolomite, that there is a very definite suggestion of the movement of sulphides out of the breccia migration channel and a precipitation on the dolomite with some replacement. The writer believes that dolomite was the flocculating agent, and the conditions may have been very similar to those created in the laboratory by Clark and Menaul. The mineralizing solutions carrying the disperse colloids probably rose relatively rapidly along vertical fractures and spread more slowly along the sandstone-conglomerate stratigraphic break. Extensive solution of the dolomite created a sufficient concentration of the electrolyte to cause flocculation of the dispersed sulphides.

²⁵ Clark and Menaul, *op. cit.*, pp. 37-41.

Boydell²⁶ calls upon a probable excess of carbon dioxide as an effective agent for putting the carbonate electrolyte into solution and thus bringing about coagulation. He also postulates dispersion by the peptizing influence of excess hydrogen sulphide. The effect of hydrogen sulphide on the carbonate is not considered. An aqueous solution of hydrogen sulphide compares favorably with carbon dioxide in solution as a solvent for carbonates. Soluble calcium hydro-sulphide and calcium bicarbonate are formed. The reaction proceeds to the right according to the equation $2\text{CaCO}_3 + 2\text{H}_2\text{S} \rightarrow \text{Ca}(\text{HS})_2 + \text{Ca}(\text{HCO}_3)_2$. Both compounds formed are fairly soluble and are effective coagulating agents. The writer sees no necessity for postulating the presence of carbon dioxide in the solutions, since hydrogen sulphide is already required as a peptizer in order to complete the process. By way of verifying the validity of the foregoing statements the writer polished a specimen of pure calcite, placed it in a bottle of distilled water, and bubbled H_2S through it for about five minutes. The bottle was then corked and allowed to stand for four hours. At the end of that time the polished surface of the calcite was examined and found to be deeply etched. Barium chloride was added to the solution in order to determine whether the etching was due to the formation of sulphuric or sulphurous acids. No sulphate or sulphite ions were detected.

If the foregoing reaction is acceptable as an explanation of the carbonate solution at the Cornwall mines, we have two simultaneously operating causes of coagulation of dispersed sulphides. One is the removal of the protecting agent, hydrogen sulphide, by a chemical reaction, and the other is the consequent production of two effective electrolytes as a result of the same chemical reaction.

Since thermal ancestry and low-temperature conditions are postulated, a distant magmatic source is necessarily inferred. How hydro-thermal mineral-bearing solutions, passing up through a zone with a wide range of temperature-pressure conditions, could escape mineral deposition constitutes a real question. The explanation is probably to be sought in a consideration of the dispersed colloidal condition of the mineral matter at the time of introduction. If we postulate the

²⁶ H. C. Boydell, "Operative Causes in Ore Deposition," *Trans. Inst. of Min. and Met.*, Vol. XXXVI (1927).

material being kept in disperse condition because of the presence of an excess of hydrogen sulphide, we can call upon five means, according to Boydell,²⁷ of inducing relatively rapid deposition of sulphide material. These coagulating causes he lists as (1) influence of electrolytes; (2) mutual reaction of two disperse phases; (3) removal of protecting agent; (4) change of temperature or/and pressure; and (5) electrolysis.

Of these the writer need appeal to but one, and recognize the probability of the partial effect of two others. One of the latter two is the expected decrease of temperature and pressure consequent upon the rise of the solutions toward the surface. The other is the loss of hydrogen sulphide. This could presumably be accomplished either by mingling of the mineralizing solutions with ground water and a resulting dilution of the hydrogen sulphide content to cause coagulation, by a gradual diffusion of hydrogen sulphide under the influence of lesser pressure conditions or through removal by reaction with the electrolyte, as discussed above. A third alternative, and perhaps the most effective, would be the coagulation of the disperse material when the solutions came into contact with an effective soluble electrolyte. The carbonates of the Powell-Cotter dolomites, as well as the small amount of aluminous material along the slight unconformities, would serve as adequate coagulators. As already stated in discussing the mineralized portions of the chert-dolomite breccia, there is definite evidence of a selective coagulation of sulphides on the dolomite fragments.

It seems plausible to the writer to think of these sulphides of colloidal origin as differentiates from a system which at its magmatic source was rich in truly dissolved sulphides and lean in dispersed colloidal sulphide material. While in transit through probable igneous wall rock there would be precipitation of mineral matter from true solutions due to temperature-pressure changes and a resulting relative concentration of the colloidal phase in the solutions, since the peptizing influence of hydrogen sulphide would prevent deposition of the finely suspended material. If the original solutions at their source were only moderately rich in hydrogen sulphide, we might conceive of certain difficultly dispersible sulphides being deposited

²⁷ *Ibid.*, p. 42.

near the source, while those species easily dispersed would move away and perhaps be completely segregated. However, there might well be slight overlaps, and small amounts of the colloidal phase might be included in the minerals deposited from true solutions. And again, if an easily coagulated material is selectively deposited, it might be expected to carry with it some of the disperse material as minute colloidal inclusions. There would, then, be complete gradations from (1) deposits of dominantly colloidal origin, with a negligible amount of material deposited from true solutions to (2) deposits dominantly derived by crystallization from high-temperature solutions, with a small amount of colloidal material hidden within growing crystals. We may in consequence have certain species of minerals which form by crystallization from true solutions closely associated with other species which exhibit every evidence of colloidal deposition. Again, we may expect some species to form into automorphic crystals directly from the disperse colloidal condition as an expression of specific ability, or we may have minerals which possess ability to go from colloidal gel condition to automorphic crystalline condition without retaining much evidence of the original gel state. Several of these specific variations are suggested in the Cornwall copper ores. Pyrite seems to have an ability to form crystals from the disperse colloidal condition as well as to crystallize from the gel condition. Etching of chalcopyrite frequently brings out crystalline texture with individual crystals transecting banded colloidal structures. Relict structures demonstrating colloidal ancestry are not always present. The fact that any are preserved is probably due to the unusually mild conditions of deposition. Under more usual moderate or extreme temperature-pressure conditions metacolloidal crystallization would be so perfect and complete that it would be exceptional to find colloidal textures preserved even though it may have been the principal mode of ore deposition.

According to Van Bemmelen, von Weimarn, and others, there is a different precipitation concentration for each electrolyte and sol.²⁸ This concentration is very much greater when the electrolyte is

²⁸ J. M. van Bemmelen, "Die Absorption," *Gesammelte Abhandlungen ueber Kolloide und Absorption*, (Theodor Steinkoff, 1926); P. P. von Weimarn, in *The Chemistry of Colloids*, by W. W. Taylor (Edinburgh, 1915).

added slowly; also flocculation is less sudden. Before the rapid flocculation stage is reached there is nothing to prevent crystallization keeping pace with flocculation, particularly in the case of such minerals as pyrite, which are known to possess strong crystallizing properties. This in substance amounts to direct crystallization from the disperse phase. Von Weimarn also states that, whereas a definite concentration of electrolyte is necessary for rapid flocculation, a further increase in concentration of the electrolyte prevents rapid coagulation. Thus in cases where there is a slow, uniform increase in concentration of an electrolyte (as there would be if production of electrolyte were due to solution of a relatively slowly soluble carbonate wall rock), there is a well-defined concentration value for the rapid deposition of the disperse material. Preceding and following this stage, coagulation would be slow and crystallization might well keep pace with flocculation. This would create automorphic crystals of some of the most easily and least easily flocculated minerals. Thus is offered a possible explanation for the early pyrite and the late sphalerite being automorphic crystalline, while the bulk of the ore shows massive colloidal textures. This would also explain why the pyrite is always included in later chalcopyrite, while sphalerite is very commonly found as drusy vug linings or embedded in the healing-solution mineral calcite. Lindgren²⁹ says concerning the colloidal origin of the Cobalt ores:

The complex gel was almost immediately transformed into crystalloids, resulting in the mixture of minerals which we now find. . . . Because the crystallization followed so closely on the heels of gel-precipitation, it is not surprising that we find places where crystals were formed directly in the country rock or in the vein filling, but they do not appear to be the principal mode of ore formation.

Presumably conditions might be such that all of the disperse ore material might be deposited before the rapid precipitation concentration was realized, in which case we would have a colloidal ore deposit composed entirely of coarsely crystalline material with almost nothing to indicate its colloidal ancestry. Only during the rapid coagulation stage would identifiable colloidal textures and structures be developed, and even these might be eliminated by meta-colloidal adjustment and crystallization under the influence of pres-

²⁹ W. Lindgren, "Metasomatism," *op. cit.*, p. 261.

sure and temperature. In the laboratory, Chrustchoff³⁰ produced quartz and tridymite crystals, both from silica sol and from silica gel, by heating in closed systems from 250° to 350° C. Tolman and Clark³¹ formed chalcocite crystals from the disperse condition, and later Young and Moore³² at a temperature of 30° C. readily produced crystals of chalcocite, covellite, chalcopyrite, and bornite by first dispersing with concentrated solutions of hydrogen sulphide.

The writer is very much in sympathy with the experimental evidence and theoretical considerations advanced by such workers as Bateman; Boydell; Clark and Menaul; Cox, Dean, and Gottschalk; Lasky; Lindgren; Tolman and Clark; and Schneiderhohn on the subject of colloidal ore deposits. The conclusions reached by Bateman and Lasky concerning the colloidal origin of the sulphide ores at Kennecott seem sound. Here they have described a type of mineral occurrence long suspected by a few workers, but previously not so conclusively linked with ascending solutions. The similarity between the Kennecott ores and those described above is very close. The mineralizing solutions apparently differed in but two respects. The iron and silica content of the Kennecott mineralizing solutions was very low, pyrite is conspicuously absent, and chalcocite is the dominant primary copper mineral; quartz is rare. At the Cornwall mines pyrite and marcasite are very abundant, and, as would be expected, chalcopyrite is the dominant copper mineral. So abundant and persistent was the iron content of the solutions that only small amounts of primary chalcocite and covellite are found.

There is no evidence of any reaction between an early coagulum and disperse material to produce a third mineral species, as described by Lasky.³³ He explains Liesegang diffusion bands of chalcopyrite and bornite as due to the diffusion of chalcocite molecules through the chalcopyrite coagulum with the resultant development of bands of bornite. Bornite associated with chalcopyrite at the Cornwall mines occurs as a matrix for globules of chalcopyrite or as interstitial mate-

³⁰ K. von Chrustchoff, *Neues Jahrbuch f. Min. Geol. u. Pal.*, Vol. I (1887), p. 205.

³¹ *Op. cit.*, p. 573.

³² S. W. Young and Neil Preston Moore, "Laboratory Studies on Secondary Sulphide Enrichment," *Econ. Geol.*, Vol. XI (1916), pp. 349-65.

³³ *Op. cit.*

rial between chalcopyrite crystals. There is every evidence that the bornite was coagulated from disperse condition as the bornite molecule. Its age relation is believed to be an expression of electronic charge on the disperse particles and is determined by the ratio of copper to iron in the molecule. It occupies its proper age position in a sequence of minerals of decreasing iron and increasing copper content.

During the progress of the study of the Missouri ores, the writer was impressed with the need of additional criteria for the recognition of colloidal textures. The conventional colloform structure, while present, was one of the least conspicuous. It is suspected by the writer that, owing to the lack of careful microscopic study, some deposits of colloidal origin may have been heretofore overlooked, and that certain unusual, uninterpreted, or ignored types of texture may prove to be colloidal in origin. The writer feels that the subject has not received enough attention, and believes further that zonal distribution of base metal sulphides may exist due to this colloidal mode of origin, as suggested by Tolman and Clark.³⁴ Sulphide deposits carrying essentially the same suite of materials, but differing widely in the ratio of these minerals to each other, may have a common origin and are but zonal expressions of the mineralization due to differential ease of dispersion and coagulation of the sulphides. Should one of a series of such deposits not show colloidal textures, we cannot assume a priori that all are not genetically related. As indicated above, ease of dispersion may just as effectively cause a species separation from a common suite as order of coagulation. One mineral may be deposited from true solution while the other more easily dispersed species may be carried on as a colloid under the influence of a peptizer such as H_2S . In this case the mineral first deposited might carry a few automorphic crystals of the second as an expression of slight crystallization from the disperse phase. The lead-zinc deposits of the Mississippi Valley, carrying some copper and associated regionally with deposits dominantly cupriferous, offer an example of a type of association which may eventually prove to be related to

³⁴ *Op. cit.*, pp. 37-41.

those here described. Emmons³⁵ has drawn an impressive picture of the zonal distribution of these ores. Cox, Dean, and Gottschalk have postulated a colloidal origin for some of the Tri-State ores, though they consider them as having been deposited from artesian waters. The Cornwall copper ores are definitely colloidal in origin and were deposited from ascending thermal solutions. It seems that any further attempt to bring the Mississippi Valley ore deposits into a single metallogenetic province should, of necessity, at least consider a colloidal explanation for the zonal distribution and segregation described by Emmons. We cannot assume that lack of dominance of colloidal textures and the existence of the idiomorphic crystalline expression of a suite of minerals conclusively indicate non-colloidal origin. It has long been known that crystallization directly from the disperse colloidal condition may take place. If it can be established that zonal distribution of sulphides exists as a function of the order of coagulation or dispersion of specific minerals, the significance and possible economic application becomes at once apparent.

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³⁵ W. H. Emmons, "The Origin of the Deposits of Sulphide Ores of the Mississippi Valley," *Econ. Geol.*, Vol. XXIV (1929), pp. 221-71.

